

# 1. Basic Statistical Mechanics

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In statistical mechanics, we consider quantum mechanical systems in which particles like atoms and electrons have different energy levels.

We want to know the probability that the particles are at each level. We can use this information to calculate the population at each level, the total energy of the system, the heat capacity, etc.

Later on, we shall learn how to calculate this probability using the Boltzmann distribution. Before that, we need to answer one question:

Even if we know the probabilities at each level, particles are often free to hop between levels. Would this not cause big changes in energy of the system?

In order to answer this question, we investigate the example where we only have 2 energy levels, and with equal probabilities.

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## Basic statistics

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To use a familiar example, think of each particle as a coin and each level as one side of the coin.

Suppose the coin is tossed 2 times. The possible outcomes are:

TT

HT

TH

HH

Let  $x$  be the number of heads. Let  $n$  be the total number of outcomes.

Let  $P(x)$  be probability of getting  $x$  heads. This is given by  $P(x) = x/n$ .

$$P(0) = 1/4$$

$$P(1) = 2/4$$

$$P(2) = 1/4$$

Suppose we toss the coin  $n$  times and record the number of H. Suppose we repeat this many times.

We would get a sample of data for  $x$ , e.g.  $\{2, 0, 1, 3, 2, 2, 3, 0, \dots\}$

In statistics, we are often interested in two numbers - the mean and the standard deviation.

The mean is the simple average.

The standard deviation tells us how much the numbers in the data deviate from the mean.

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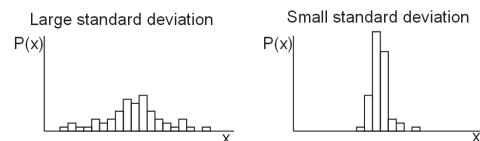
When the standard deviation is small

The standard deviation is relevant to the idea of macrostates that we want to develop.

We are particularly interested in what it means if the standard deviation becomes very small.

Recall that the standard deviation is a measure of the average deviation of  $x$  from the mean.

So if the standard deviation is small, it means that most of the data is very close to the mean value.



If we look at a histogram of the data, it would look more sharply peaked.

If we know the probability distribution  $P(x)$ , we can also calculate the mean and standard deviation without actually tossing the coin.

The mean is given by

$$\mu = \sum xP(x).$$

The standard deviation is the root mean square of  $x - \mu$ . So it is essentially a kind of average of how much  $x$  deviates from  $\mu$ .

It is given by

$$\sigma = \sqrt{\sum (x - \mu)^2 P(x)}.$$

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The binomial distribution

Let  $p$  be probability of getting a Head, and  $q$  the probability of getting a Tail.

If we have a fair coin, then  $p = q = 1/2$ .

Suppose we toss a coin  $N$  times.

The probability of getting  $x$  heads is given by the binomial distribution:

$$P(x) = {}^N C_x p^x q^{N-x}.$$

When we toss a coin  $N$  times, suppose that we get  $x$  heads.

When we toss  $N$  times again, we may get a different  $x$ .

The mean value of  $x$  is given by a sum over  $x$ , weighted by the probabilities:

$$\mu = \sum_{x=0}^N xP(x) = Np.$$

The standard deviation is given by:

$$\sigma = \sqrt{\sum_{x=0}^N (x - \mu)^2 P(x)} = \sqrt{Npq}.$$

Both formulae can be derived by substituting the binomial distribution  $P(x) = {}^N C_n p^n q^{N-n}$ .

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### A reference quantity

The reason is because, on the graph, we are looking at the standard deviation relative to the total number of coins  $N$ .

So, although 10 is large than 1,  $10/400$  would be smaller than  $1/4$ .

In the case of the coins, we should therefore be comparing the standard deviation with the total number of coins  $N$ .

$x$  is the actual number of heads.

The average of deviation of this number from the mean, as a fraction of  $N$ , is  $\sigma/N = \sqrt{pq/N}$ .

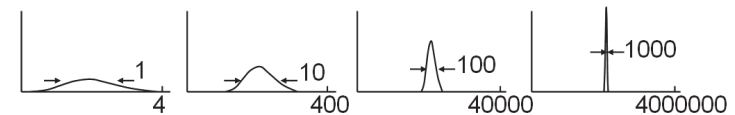
When  $N$  is very large, this fraction approaches zero.

Lets get some idea of how  $\sigma$  changes a  $N$  is increased. For a fair coin  $p = q = 1/2$ .

$N$	$\sigma (= \sqrt{Npq})$
4	1
400	10
40000	100
4000000	1000

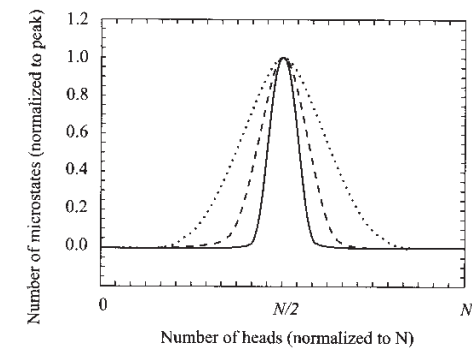
It looks like the number of heads changes more from one toss to the next, as the number of coins is increased.

But if we plot the distribution on a graph:



we would find that it gets more sharply peaked!

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The dotted curve is the smallest  $N$ , the solid curve the largest  $N$ . Notice that the peak gets narrower for large  $N$ .

If  $N$  is as big as the number of atoms in a real material, the peak becomes extremely narrow.

Then  $x = N/2$  becomes almost the only possible value.

We can apply this to atoms:

1. H is the higher energy state, T is the lower one.
2. One toss of a coin is one atom.
3. The larger the number of H, the higher the temperature.

In a real material at room temperature, atoms could hop between energy levels randomly through colliding with other atoms.

Because the number of atoms is huge, deviation of particle numbers at each level from the values predicted from their probabilities are extremely small.

### Exercise 1

How many atoms are there in each of the following?

( $N_A = 6.022 \times 10^{23}$ )

- 1) 1 mole of iron
- 2) 0.2 mole of copper
- 3) 3 moles of silver
- 4) 1 mole of oxygen ( $O_2$ ), and how many molecules?
- 5) 1 mole of water ( $H_2O$ ), and how many oxygen atoms?
- 6) 1 mole of sodium chloride ( $NaCl$ ), and how many sodium ions?
- 7) 1 mole of helium-4 ( $^4He$ )
- 8) 1 mole of helium-3 ( $^3He$ )

### Warming up exercises

### Solutions to Exercise 1

- 1)  $6.022 \times 10^{23}$
- 2)  $0.2 \times 6.022 \times 10^{23}$
- 3)  $3 \times 6.022 \times 10^{23}$
- 4)  $2 \times 6.022 \times 10^{23}$  atoms, and  $6.022 \times 10^{23}$  molecules
- 5)  $3 \times 6.022 \times 10^{23}$  atoms, and  $6.022 \times 10^{23}$  oxygen atoms
- 6)  $2 \times 6.022 \times 10^{23}$  atoms, and  $6.022 \times 10^{23}$  sodium ions
- 7)  $6.022 \times 10^{23}$
- 8)  $6.022 \times 10^{23}$

**Exercise 2**

What is the mass of each of the following? ( $A_r$  stands for relative atomic mass.)

- 1) 1 mole of iron ( $A_r=56$ )
- 2) 0.2 mole of copper ( $A_r=64$ )
- 3) 3 moles of silver ( $A_r=108$ )
- 4) 1 mole of oxygen ( $O_2$ ) ( $A_r=16$ )
- 5) 1 mole of water ( $H_2O$ ) ( $A_r$  of H=1, of O=16)
- 6) 1 mole of sodium chloride (NaCl) ( $A_r$  of Na=23, of Cl=35.5)
- 7) 1 mole of helium-4 ( $^4He$ )
- 8) 1 mole of helium-3 ( $^3He$ )

**Exercise 3**

How many atoms are there in each of the following? ( $A_r$  stands for relative atomic mass.)

- 1) 1 g of iron ( $A_r=56$ )
- 2) 1 g of copper ( $A_r=64$ )
- 3) 1 g of silver ( $A_r=108$ )
- 4) 1 g of oxygen ( $O_2$ ) ( $A_r=16$ )
- 5) 1 g of water ( $H_2O$ ) ( $A_r$  of H=1, of O=16)
- 6) 1 g of sodium chloride (NaCl) ( $A_r$  of Na=23, of Cl=35.5)
- 7) 1 g of helium-4 ( $^4He$ )
- 8) 1 g of helium-3 ( $^3He$ )

**Solutions to Exercise 2**

- 1) 56 g
- 2)  $0.2 \times 64$  g
- 3)  $3 \times 108$  g
- 4)  $2 \times 16$  g
- 5)  $(2 \times 1 + 16)$  g
- 6)  $(23 + 35.5)$  g
- 7) 4 g
- 8) 3 g

**Solutions to Exercise 3**

- 1)  $1/56 \times 6.022 \times 10^{23}$
- 2)  $1/64 \times 6.022 \times 10^{23}$
- 3)  $1/108 \times 6.022 \times 10^{23}$
- 4)  $1/(2 \times 16) \times 6.022 \times 10^{23}$
- 5)  $1/(1 + 1 + 16) \times 6.022 \times 10^{23}$
- 6)  $1/(23 + 35.5) \times 6.022 \times 10^{23}$
- 7)  $1/4 \times 6.022 \times 10^{23}$
- 8)  $1/3 \times 6.022 \times 10^{23}$

**Exercise 4**

Suppose a biased coin is tossed 2 times. The probability distribution for 0, 1 and 2 heads are given by 0.36, 0.48 and 0.16, respectively. Find the mean and standard deviation of the number of heads.

**Answer**

Let  $x$  be the number of heads. The distribution given is

$x$	$P(x)$
0	0.36
1	0.48
2	0.16

**Microstates and Macrostates**

The mean is  $\mu = \sum xP(x) = 0 \times 0.36 + 1 \times 0.48 + 2 \times 0.16 = 0.8$ .

(Out of 2 tosses, we only get 0.8 heads on average. Obviously, this coin is biased towards the tail.)

$x$	$x - \mu$	$(x - \mu)^2$
0	-0.8	0.64
1	0.2	0.04
2	1.2	1.44

The standard deviation is

$$\sigma = \sqrt{\sum (x - \mu)^2 P(x)}$$
$$= \sqrt{0.64 \times 0.36 + 0.04 \times 0.48 + 1.44 \times 0.16} = 0.48.$$

Consider a particle with 2 energy levels:  $\varepsilon_1$  and  $\varepsilon_2$ . Suppose we have  $N = 2$  particles. And there are  $n_1$  particles at energy level  $\varepsilon_1$ , and  $n_2$  at  $\varepsilon_2$ .

The following lists all the possible arrangements:

Macrostates    Microstates

(2, 0)	$[\varepsilon_1, \varepsilon_1]$
(0, 2)	$[\varepsilon_2, \varepsilon_2]$
(1, 1)	$[\varepsilon_1, \varepsilon_2], [\varepsilon_2, \varepsilon_1]$

For example,  $[\varepsilon_1, \varepsilon_2]$  would mean that particle 1 is at level  $\varepsilon_1$  and particle 2 is at level  $\varepsilon_2$ . This is one particular arrangement.

A particular arrangement of particles among energy levels is called a **microstate**.

$(n_1, n_2)$  specifying the number of atoms at each level.

The set of numbers specifying the number of atoms at each level is called the **macrostate**.

E.g. Consider a particle with 3 energy levels:  $\varepsilon_1$ ,  $\varepsilon_2$  and  $\varepsilon_3$ . Suppose there are  $N = 2$  particles. And there are  $n_1 = 2$  at energy level  $\varepsilon_1$ ,  $n_2 = 0$  at  $\varepsilon_2$ , and  $n_3 = 0$  at  $\varepsilon_3$ .

The macrostate in this case is  $(n_1, n_2, n_3) = (2, 0, 0)$ .

Lets write down a useful relation:

$$N = n_1 + n_2 + n_3$$

The total number of particles is equal to the sum of the particles at each level.

For more energy levels, the formula generalises to:

$$\Omega = \frac{N!}{n_1!n_2!n_3!\dots n_i!\dots}$$

or

$$\Omega = \frac{N!}{\prod_i n_i!}$$

The total number of particles is  $N$ . The macrostate is specified by the number of particles at each energy level:  $(n_1, n_2, \dots, n_i, \dots)$ . So the total number must be the sum of the particles at each level:

$$N = \sum_i n_i$$

We consider an isolated system that is very well insulated from the surrounding. Then the total energy  $U$  of the particles would remain constant.

In general, a system can have many energy levels. We want to know the most likely macrostate  $(n_1, n_2, n_3, \dots)$  of a system, because this would allow us to find the total energy, heat capacity, etc.

The most likely macrostate is the one with the largest number of microstates - or arrangements.

For two energy levels, the number of microstates for the macrostate  $(n_1, n_2)$  is

$$\Omega = \frac{N!}{n_1!n_2!}$$

It is the number of ways of putting  $N$  different objects into 2 boxes.

There are  $n_1$  particles at energy level  $\varepsilon_1$ , so the total energy of these particles is  $n_1\varepsilon_1$ . Adding up the energy of the particles at all energy levels, we have the energy of the whole system:

$$U = \sum_i n_i \varepsilon_i$$

$\Omega$  is a function of the variables  $(n_1, n_2, \dots)$ .

There are 2 conditions, or constraints, on these variables:

- (i) the total number of particles is a constant, and
- (ii) the total energy is also a constant.

In order to maximise  $\Omega$ , we can use the method of Lagrange multipliers.

The procedure is as follows:

1. We maximise  $\ln \Omega$  instead of  $\Omega$ . The result would be the same because when  $\ln \Omega$  is a maximum, so is  $\Omega$ .
2. The reason for using  $\ln \Omega$  is that it can be simplified for very large  $N$  using the Stirling's theorem.
3. Write down the Lagrange function  $\ln \Omega + \lambda_1 N + \lambda_2 U$ .
4.  $\alpha$  and  $\beta$  are new parameters called Lagrange multipliers.
5. Differentiate this with respect to every  $n_i$ .
6. Set the derivative to zero and solve for  $n_i$ ,  $\lambda_1$  and  $\lambda_2$ .
7. This gives the macrostate  $(n_1, n_2, \dots)$ .

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The algebra

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We need to maximise

$$\ln \Omega + \lambda_1 N + \lambda_2 U$$

In order to do so, we need to differentiate this. Start with

$$N = n_1 + n_2 + \dots + n_i + \dots$$

Differentiating with respect to  $n_i$  gives

$$\frac{\partial N}{\partial n_i} = 1.$$

Next, we differentiate

$$U = n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_i \epsilon_i + \dots$$

This gives

$$\frac{\partial U}{\partial n_i} = \epsilon_i.$$

Next we need to differentiate  $\ln \Omega$ .

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The Stirling's Theorem is used for large factorials.

For real objects,  $N$  may be the number of atoms. This could be as big as  $10^{30}$ , and it takes a long time to calculate.

Fortunately, there is a simple, approximate formula that is very accurate for large numbers:

$$\ln N! \approx N \ln N - N$$

This formula is the Stirling's Theorem.

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The algebra

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Start with the formula

$$\Omega = \frac{N!}{n_1! n_2! \dots n_i! \dots}$$

Then take the logarithm,

$$\ln \Omega = \ln N! - \ln n_1! - \ln n_2! - \dots - \ln n_i! - \dots$$

and apply Stirling's theorem:

$$\ln \Omega = N \ln N - N - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - \dots - (n_i \ln n_i - n_i) - \dots$$

Differentiating, we get

$$\frac{\partial \ln \Omega}{\partial n_i} = -\ln n_i$$

Note that in this differentiation,  $N$  in  $\Omega$  is to be treated as a constant. This is unlike in  $\lambda_1 N$  where it is a function of  $n_i$ .

The reason is because  $\Omega$  is up to us to define, and it is sufficient to vary  $n_i$ .

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These are what we have obtained:

$$\begin{aligned}\frac{\partial N}{\partial n_i} &= 1 \\ \frac{\partial U}{\partial n_i} &= \epsilon_i \\ \frac{\partial \ln \Omega}{\partial n_i} &= -\ln n_i\end{aligned}$$

To maximise the Lagrange function  $\ln \Omega + \lambda_1 N + \lambda_2 U$ , we need to differentiate this and set the derivative to zero:

$$\frac{\partial \ln \Omega}{\partial n_i} + \lambda_1 \frac{\partial N}{\partial n_i} + \lambda_2 \frac{\partial U}{\partial n_i} = 0$$

Substituting the above results, we get:

$$\ln n_i + \lambda_1 + \lambda_2 \epsilon_i = 0$$

Next, we need to find  $\lambda_2$ . In principle, we can use the next constraint

$$U = \sum n_i \epsilon_i$$

Substituting the solution

$$n_i = A \exp(\lambda_2 \epsilon_i)$$

we get

$$U = \sum A \epsilon_i \exp(\lambda_2 \epsilon_i)$$

Then solve for  $\lambda_2$ .

Unfortunately, this equation is very difficult to solve. Instead, we need to take another approach. That is to make use of our knowledge of thermodynamics.

We have obtained

$$\ln n_i + \lambda_1 + \lambda_2 \epsilon_i = 0$$

Solving for  $n_i$  gives the solution:

$$n_i = A \exp(\lambda_2 \epsilon_i)$$

where  $A = \exp(\lambda_1)$ .

Next, we need to determine  $\lambda_1$ , or  $A$ , and  $\lambda_2$ .

$A$  can be obtained using

$$N = \sum n_i,$$

the condition that the total number of particles is  $N$ . This is called the normalisation condition. Substituting, we get

$$N = A \sum \exp(\lambda_2 \epsilon_i).$$

Rearranging this gives

$$A = \frac{N}{\sum \exp(\lambda_2 \epsilon_i)}.$$

The purpose of doing all these calculations is to find a way to calculate thermodynamic quantities like entropy and heat from first principles.

Instead of solving for  $\lambda_2$  directly, we can try and find it in terms of known quantities in thermodynamics. We shall start by stating the result:

$$\lambda_2 = -\frac{1}{k_B T}.$$

where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. There are different ways to determine this. We shall look at the following approach.

Since  $N$  is constant,  $dN = 0$ . So

$$d(\ln \Omega) + \lambda_1 dN + \lambda_2 dU = 0$$

becomes

$$dU = -\frac{1}{\lambda_2} d(\ln \Omega)$$

Compare with

$$dU = T dS.$$

Boltzmann postulated that

$$S = k_B \ln \Omega$$

where  $k_B$  is a constant. Substituting this into the above, we find that

$$\lambda_2 = -\frac{1}{k_B T}$$

This completes the solution for the macrostate  $(n_1, n_2, \dots)$ :

$$n_i = A \exp(\lambda_2 \varepsilon_i) = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

To relate  $\lambda_2$  to the entropy formula

$$dQ = dU = T dS,$$

we look at the Lagrange function  $\ln \Omega + \lambda_1 N + \lambda_2 U$  again.

Previously, we have taken the derivative to find the set of numbers  $(n_1, n_2, \dots)$  that would maximise the function. We have found the solution for  $n_i$ , except for the unknown  $\lambda_2$ .

For small variations about this solution  $(n_1, n_2, \dots)$ , the change in the Lagrange function would be zero, since it is at a maximum. So

$$d(\ln \Omega) + \lambda_1 dN + \lambda_2 dU = 0$$

Suppose we impose the condition that the total  $N$  is fixed, but we give some heat to the system so that  $U$  increases a little.

We shall see later, in the lectures on ideal gas, that  $k$  is the Boltzmann constant

$$k_B = \frac{R}{N_A} = 1.3807 \times 10^{-23} \text{ J K}^{-1},$$

where  $R$  is the ideal gas constant and  $N_A$  is Avogadro's constant.

The solution for the macrostate tells us how the number of particles are distributed in different energy levels:

$$n_i = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right).$$

It is called the Boltzmann distribution.

Historically, the formula

$$S = k_B \ln \Omega.$$

was first postulated by Boltzmann. It is so important that it is engraved on his tombstone ...



### Example 1

Minimise the function  $f(x, y) = x^2 + y^2$ , subject to the constraint  $x + y - 2 = 0$ .

- (i) Do it mentally, or by inspection of the graphs.
- (ii) Do it using Lagrange multiplier.

Do the results agree?

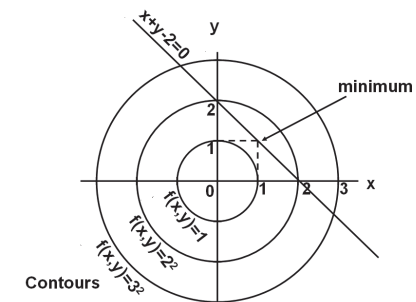
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### Worked Examples

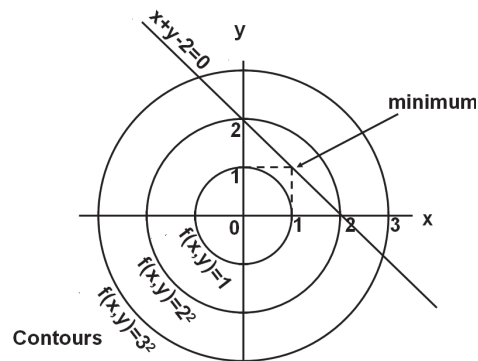
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Mentally ...

### Answer



1. The contours of  $f(x, y)$  are just circles, e.g.  $x^2 + y^2 = 1$ ,  $x^2 + y^2 = 2$ , ... The circles get larger as the value increases.
2. The constraint  $x + y - 2 = 0$  is a straight line with intercepts  $x = 2$  or  $y = 2$ .



1. By symmetry,  $f(x, y)$  is highest at the midpoint between the intercepts, where  $x = y = 1$ .
2. Therefore,  $f(x, y) = 1^2 + 1^2 = 2$ .

### Example 2

Use your calculator to work out  $\ln 10!$ . Compare your answer with the simple version of Stirling's theorem ( $N \ln N - N$ ). How big must  $N$  be for the simple version of Stirling's theorem to be correct to within (ii) 5% (ii) 1% ?

### Answer

$\ln(10!) = 15.11$  whereas  $10 \ln(10) - 10 = 13.03$ . There is less than 5% difference for  $N = 24$  and less than 1% for  $N = 91$ . Stirling's approximation is quite accurate even for relatively small  $N$ .

1. Let  $g(x, y) = x + y - 2$ . The constraint is then  $g(x, y) = 0$ .
2. The Lagrange function is

$$f(x, y) + \lambda g(x, y) = x^2 + y^2 + \lambda(x + y - 2) \quad (1)$$

3. The gradient gives:
  1. Differentiate wrt  $x$ :  $2x + \lambda = 0$ .
  2. Differentiate wrt  $y$ :  $2y + \lambda = 0$ .
4. Solving with the constraint equation gives  $\lambda = -2$  and  $x = y = 1$ , as before.

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### Boltzmann Distribution

### Example 3

A system of particles is at a temperature of 2 K. Find the Boltzmann factor for each of these energy levels: ( $k_B = 1.38 \times 10^{-23}$ )

- 1)  $1 \times 10^{-23}$  J
- 2)  $2 \times 10^{-23}$  J
- 3)  $3 \times 10^{-23}$  J
- 4)  $4 \times 10^{-23}$  J
- 5)  $5 \times 10^{-23}$  J
- 6)  $6 \times 10^{-23}$  J
- 7)  $7 \times 10^{-23}$  J
- 8)  $8 \times 10^{-23}$  J

**Solutions to Example 3**

- 1) 0.6961
- 2) 0.4845
- 3) 0.3372
- 4) 0.2347
- 5) 0.1634
- 6) 0.1137
- 7) 0.07916
- 8) 0.05510

**Solutions to Example 4**

- 1)  $6.736 \times 10^{22}$
- 2)  $5.896 \times 10^{22}$
- 3)  $5.601 \times 10^{22}$
- 4)  $5.452 \times 10^{22}$
- 5)  $5.362 \times 10^{22}$
- 6)  $5.302 \times 10^{22}$
- 7)  $5.259 \times 10^{22}$
- 8)  $5.226 \times 10^{22}$

**Example 4**

There are  $10^{23}$  particles. The system has two energy levels only: 0 J and  $10^{-23}$  J. Find the number of particles at 0 J when the temperature is:

- 1) 1 K
- 2) 2 K
- 3) 3 K
- 4) 4 K
- 5) 5 K
- 6) 6 K
- 7) 7 K
- 8) 8 K

**Example 5**

Consider a 10000 distinguishable particles at room temperature, 298 K. Suppose that each particle has 2 energy levels, 0.01 eV and 0.02 eV. Find the number of the particles in each energy level. ( Boltzmann's constant is  $1.3807 \times 10^{-23} \text{ J K}^{-1}$ .)

**Answer**

Since the number is quite large, we assume that the probability at each energy level is given by Boltzmann's distribution  $A \exp(-\varepsilon/k_B T)$ .

At 0.01 eV,  $A \exp(-\varepsilon/k_B T) = 0.6778A$ .  
 At 0.21 eV,  $A \exp(-\varepsilon/k_B T) = 0.4594A$ .  
 The total is  $0.6778A + 0.4594A = 10000$ . So  $A = 8794$ .

Therefore the numbers are:

at 0.01eV,  $0.6778 \times 8794 = 5961$ ;  
 at 0.02eV,  $0.4594 \times 8794 = 4040$ .

**Example 7**

Consider a large number of distinguishable particles, at temperature  $T$ . Each particle has 4 energy levels 0,  $k_B T$ ,  $2k_B T$  and  $3k_B T$ . Calculate the fraction of particles in each energy level.

**Answer**

Since the number is quite large, we assume that the probability at each energy level is given by Boltzmann's distribution  $A \exp(-\varepsilon/k_B T)$ .

**Example 6**

Calculate the quantity  $k_B T$  at room temperature, 298 K. Give the answer in eV. ( Boltzmann's constant is  $1.3807 \times 10^{-23}$  J  $K^{-1}$ . Electron charge is  $1.6 \times 10^{-19}$  C.)

**Answer**

In Joules,  $k_B T = 1.3807 \times 10^{-23} \times 298 = 4.114 \times 10^{-21}$  J.

In eV,  $k_B T/e = 4.114 \times 10^{-21}/1.6 \times 10^{-19} = 0.026$  eV.

Note: Since  $1/40 = 0.025$  is quite close to this answer,  $k_B T$  at room temperature is often quoted as  $1/40$  eV.

First, calculate the following:

at energy 0,  $\exp(-\varepsilon/k_B T) = \exp(0) = 1$ .  
 at energy  $k_B T$ ,  $\exp(-\varepsilon/k_B T) = \exp(-1) = 0.3679$ .  
 at energy  $2k_B T$ ,  $\exp(-\varepsilon/k_B T) = \exp(-2) = 0.1353$ .  
 at energy  $3k_B T$ ,  $\exp(-\varepsilon/k_B T) = \exp(-3) = 0.0498$ .

The sum is 1.553. The fractions are, therefore:

at energy 0,  $1/1.553 = 0.6439$ .  
 at energy  $k_B T$ ,  $0.3679/1.553 = 0.2369$ .  
 at energy  $2k_B T$ ,  $0.1353/1.553 = 0.0871$ .  
 at energy  $3k_B T$ ,  $0.0498/1.553 = 0.0321$ .

Notice that fraction drops to nearly  $1/10$  after just  $2k_B T$ .

In statistical mechanics, we often want to know if an energy level is likely to be populated at some temperature. If the level is much higher than  $k_B T$ , then it is unlikely to be occupied.

### Example 8

There is one mole of atoms at a temperature of 1 K. Each atom has energy levels  $-10^{-23}$  J and  $10^{-23}$  J. Find the number of atoms at each level.

#### Solution

The formula is Boltzmann distribution

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

Given

$$\varepsilon_1 = -10^{-23} \text{ J}, \varepsilon_2 = 10^{-23} \text{ J}, \text{ and } T = 1 \text{ K}.$$

We also know that  $n_1 + n_2 = N_A$  (Avogadro constant).

We need to find the numbers  $n_1$  and  $n_2$ . But what is  $A$ ?

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### Example 9

Following from the previous example, find the total energy of the atoms.

#### Solution

There are  $n_1$  atoms with energy  $\varepsilon_1$ , so the energy of these atoms is  $n_1 \varepsilon_1$

There are  $n_2$  atoms with energy  $\varepsilon_2$ . so the energy of these atoms is  $n_2 \varepsilon_2$ .

Therefore the total energy is

$$U = n_1 \varepsilon_1 + n_2 \varepsilon_2.$$

Using the values from the previous example, we get

$$U = (4.876 \times 10^{23})(-10^{-23}) + (1.145 \times 10^{23})(10^{-23}) = 6.021 J.$$

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Lets write out all equations:

$$n_1 + n_2 = N_A$$

$$n_1 = A \exp(-\varepsilon_1/k_B T)$$

$$n_2 = A \exp(-\varepsilon_2/k_B T)$$

There are three unknowns:  $n_1$ ,  $n_2$  and  $A$ . Divide the last two equations:

$$\frac{n_1}{n_2} = \exp((\varepsilon_2 - \varepsilon_1)/k_B T).$$

Let this above fraction be  $r$ . So the total is  $N_A$  is divided into the ratio  $r : 1$ . Therefore

$$n_1 = \frac{r}{r + 1} \times N_A = 4.876 \times 10^{23}$$

$$n_2 = \frac{1}{r + 1} \times N_A = 1.145 \times 10^{23}$$

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### Example 10

Following from the previous example, find the probability that an atom is at level 1, and the probability that it is at level 2.

#### Solution

The total number of atoms is  $N_A$ .

There are  $n_1$  atoms at level 1 and  $n_2$  atoms at level 2.

An atom can change level with time. So any one time, probability that it is at level 1 is

$$\frac{\text{number of possible atoms at level 1}}{\text{total number of atoms}} = \frac{n_1}{N_A} = \frac{4.876 \times 10^{23}}{6.022 \times 10^{23}}$$

Probability that it is at level 2 is

$$\frac{\text{number of possible atoms at level 2}}{\text{total number of atoms}} = \frac{n_2}{N_A} = \frac{1.145 \times 10^{23}}{6.022 \times 10^{23}}$$

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**Example 11**

There are a number of atoms at a temperature of 1 K. Each atom has energy levels  $-10^{-23}$  J and  $10^{-23}$  J. Find the probability that an atom is at each level.

**Solution**

This time, we are not given the total number of particles. We still have the Boltzmann distribution:

$$n_1 = A \exp(-\varepsilon_1/k_B T)$$

$$n_2 = A \exp(-\varepsilon_2/k_B T)$$

but we cannot find  $A$  if we don't know the the total number of particles.

But we know that the probability that an atom is at level 1 is

$$\frac{\text{number of possible atoms at level 1}}{\text{total number of atoms}} = \frac{n_1}{n_1 + n_2}$$

If we substitute the Boltzmann distribution,  $A$  cancels out!

$$\frac{n_1}{n_1 + n_2} = \frac{A \exp(-\varepsilon_1/k_B T)}{A \exp(-\varepsilon_1/k_B T) + A \exp(-\varepsilon_2/k_B T)}$$

We do know the energy levels and temperature, so we can not calculate this. In the same way, the probability that an atom is at level 2 is

$$\frac{n_2}{n_1 + n_2} = \frac{A \exp(-\varepsilon_2/k_B T)}{A \exp(-\varepsilon_1/k_B T) + A \exp(-\varepsilon_2/k_B T)}$$

The answers are 4.876/6.022 and 1.145/6.022 respectively.